

## SWELLING PRETREATMENT OF COALS FOR IMPROVED LIQUEFACTION

Levent Artok, Harold H. Schobert, Gareth D. Mitchell\* and Alan Davis\*  
Fuel Science Program and Energy and Fuels Research Center\*  
The Pennsylvania State University  
University Park, Pa 16802

Keywords: Molybdenum sulfide catalyst, catalyst dispersion, coal swelling, low severity liquefaction.

### INTRODUCTION

The organic fraction of coal can be considered to be a large three-dimensional crosslinked macromolecular network of aromatic clusters connected by etheric and aliphatic bridges with the lower molecular weight species trapped in both open and closed pores or weakly bound to the network<sup>1-2</sup>. The coal network can be swollen using appropriate solvents, leading to the expansion of the pores in it. The extent of swelling is rank-dependent. The swelling of coal facilitates impregnation of catalysts and diffusion of reagents towards the reactive sites of coal. Therefore, it can be presumed that the swelling as a pretreatment operation may increase conversion and quality of yield obtained from liquefaction.

Rincon and Cruz<sup>3</sup> found that the conversion of a Colombian coal increased when it is swollen with tetrahydrofuran (THF). Joseph<sup>4</sup> determined a direct correlation between the extent of preswelling and the conversion of coal under liquefaction conditions.

In our work, the effect of swelling on liquefaction has been investigated with and without catalyst at a pretreatment temperature of 275°C using  $(\text{NH}_4)_2\text{MoS}_4$  [ATTM] as a catalyst precursor. In addition, the activities of ATTM and  $\text{MoS}_3$  catalyst precursors were compared for unswollen coals at 275°C.

### EXPERIMENTAL

#### Coal preparation

Samples of Blind Canyon high volatile bituminous coal (PSOC-1503 and DECS-6) and Big Brown Texas lignite (PSOC-1444 and DECS-1) collected at different dates were used for this work. The origin and analyses of the coals are given in Table 1. The coals were ground without drying to minus 60 mesh and stored under a nitrogen atmosphere.

#### Catalyst preparation

ATTM was synthesized in our laboratory following the procedure of Naumann<sup>5</sup>. Molybdenum trisulfide was prepared by acidifying an aqueous solution of ATTM with formic acid, followed by washing the precipitate and drying at 110°C in a vacuum oven.

Sulfur analysis of the molybdenum compounds was performed by the Penn State Materials Characterization Laboratory using a Leco iodimetric titration sulfur analyzer and in the Penn State Combustion Laboratory using a Leco Model SC-132 sulfur analyzer. Carbon, hydrogen, nitrogen analyses were performed using a Leco Model CHN-600 elemental analyzer. Molybdenum analysis and water analysis by the Karl Fisher method were performed by Galbraith Laboratories, Inc. Elemental values and water content of samples are given in Table 2.

#### Measurement of swelling ratio

One gram of air-dried coal (PSOC-1444 and PSOC-1503) was placed in a 15 ml conical graduated screw-top centrifuge tube and centrifuged at 2900 rpm for 10 minutes and the height of the coal in the tube was recorded in ml/g. Twelve ml of solvent was added to the coal in two increments. The first 6 ml was combined with the coal and the mixture was stirred carefully until all the coal particles were wetted, then

the remaining solvent was added and the tube was sealed with a cap. After a period of time (6-30h) the tube was centrifuged again at 2900 rpm for 10 min and the height was recorded. The volumetric swelling ratio is defined as  $Q = h_2/h_1$ , where  $h_1$  = height of unswollen coal and  $h_2$  = height of swollen coal.

#### The swelling procedure of coals

The coal samples (DECS-1 and DECS-6) were swollen using methanol, pyridine, THF and 10% tetrabutylammonium hydroxide (TBAH) solution of 1:1 (v/v) ratio water:methanol mixture. The coal samples, which were predried at 110°C in vacuum, were mixed with the swelling reagent to give approximately a solvent-to-coal ratio of 3:1 (v/w) and were stirred for 6 hours under nitrogen. The solvent was removed and dried at 50°C in vacuum. In the case of pyridine, the sample was dried at 100°C in vacuum in an attempt to remove pyridine completely. In the case of TBAH, a TBAH solution was added to undried coal and only methanol and water of the mixture were removed, so that TBAH was retained in the swollen coal matrix.

#### Impregnation of swollen and unswollen coals with catalyst precursors

The catalyst precursor was loaded onto the coal in an amount based on 1% molybdenum (as the metal, not the molybdenum compound) on a dry ash free (daf) basis regardless of whether the coal had been swollen or not. Unswollen coals were impregnated with a water solution of ATTM or suspension of molybdenum trisulfide. The procedure consisted of dissolving or suspending the molybdenum salts in enough distilled water to give an approximate water-to-coal ratio of 1:1 (v/w). Then this solution or suspension was added to the coal sample and stirred 30 min before solvent removal. Excess water was removed from the mixture at room temperature in vacuum. The mixture was continuously being stirred during this procedure. Subsequently, the mixture was quenched in a dry ice-acetone bath until it became frozen and was then freeze dried, followed by vacuum drying at room temperature.

In the case of swollen coal, the swelling reagent (except TBAH) was removed in vacuum at room temperature. While the coal was still wet with swelling reagent, enough ATTM solution (which had been prepared by dissolving ATTM in 1:1 (v/v) ratio methanol:water mixture) to give solution-to-coal ratio of 1:1 (v/w) was added to coal and stirred for 30 min. In the case of TBAH, ATTM was dissolved in a 10% TBAH solution of 1:1 ratio (v/v) water:methanol mixture, then this solution was added to undried coal and stirred for 6 hours in order to give enough time for swelling of coal under nitrogen. After stirring, excess solvent was removed at room temperature in vacuum while it was continuously being stirred, and finally vacuum drying was applied at 50°C for the coals swollen with methanol, THF or TBAH, or at 100°C for pyridine-swollen coal. TBAH was allowed to remain in the coal.

The TBAH content of samples, whether catalyst-impregnated or not, was calculated from the increase of the nitrogen content of the coals, measured with a Leco Model CHN-600 analyzer.

#### Liquefaction reaction and yield fractionation

The liquefaction reactions were performed in horizontal microautoclave reactors (tubing bomb) of nominal 25 ml capacity. The procedure was the same for both preswollen and unswollen coals and also the same whether they had been impregnated with a catalyst or not.

Five grams of each prepared coal sample and five grams of phenanthrene were placed in the tubing bomb. After mixing the contents with a spatula, the reactor was sealed, pressurized to 1000 psi with nitrogen and checked for leaks. The depressurized tubing bomb was purged with hydrogen twice, pressurizing and depressurizing to 1000 psi. Subsequently, the tubing bombs, pressurized to 1000 psi with hydrogen, were attached to a vertically oscillating system fluidized sand bath which was heated to 283 °C. Immediately after the tubing bombs were placed in the sand bath, the thermostat was reset to 275°C, which was the desired pretreatment temperature. The tubing bombs attained a temperature of 275 °C in about 30 seconds. All the pretreatment experiments were done in duplicate 30 min. reaction times. During this period, the tubing bombs were oscillated through an amplitude of 2 cm at 350 cycles/min.

At the end of the reaction, the reactors were rapidly quenched to room temperature by immersion in cold water. After venting the gas, the contents of each bomb were quantitatively washed into a tared ceramic thimble using toluene and Soxhlet extracted with toluene under nitrogen until the solvent appeared colorless. The toluene extract was concentrated to 10-20 ml by rotary evaporation. The extract was diluted with 400 ml of hexane. The mixture was stirred for 1 h and asphaltenes were allowed to settle overnight and separated with 0.45 micron filter. The filtrate containing hexane-solubles was evaporated by rotary evaporation to remove the hexane. Toluene insolubles were Soxhlet-extracted with THF to separate preasphaltenes and the solid residue under nitrogen atmosphere. THF was removed from the extract by rotary evaporation. Preasphaltenes, asphaltenes and residue were dried overnight in vacuum at 110°C. The conversion was calculated by subtracting residue weight (catalyst corrected) from the weight of coal and dividing by the daf weight of the coal. It was assumed that the catalyst precursor transformed to the same product as ATTM processed without coal in hydrogen at 275°C (Table 2).

## RESULTS AND DISCUSSION

### Swelling of coals

Solvent swelling ratios with contact time for four different solvents are given in Tables 3 and 4 for Texas lignite (PSOC-1444) and the Blind Canyon hvCb (PSOC-1503), respectively. The maximum level of swelling was attained within 6 h; additional solvent-coal contact in excess of 26 h did not produce a significant increase in swelling ratio. The level of swelling experienced for each coal was slightly different with respect to the individual solvents. For the Texas lignite, swelling increased in order of methanol < THF < pyridine < 10% TBAH; for the Blind Canyon hvCb coal the order was 10% TBAH < methanol < THF < pyridine. Note that the level of the swelling for the different solvents appears to be rank-dependent. Lignites are more crosslinked than bituminous coals. Therefore, lignites give less swelling and extractability for methanol, THF and pyridine than bituminous coals. Lignites have more acidic functional groups (phenolic hydroxyl and carboxylic groups) than bituminous coals; therefore, swelling of lignite increases with increasing basicity of solvents. TBAH is quite basic and has been shown to react strongly with the types of oxygen functionalities in most lower rank coals<sup>6</sup>. Joseph<sup>4</sup> determined for the Illinois #6 bituminous coal that the highest swelling was obtained with 15% TBAH compared with those of THF and methanol. This can be explained, in part by the much higher oxygen functionality of the Illinois #6 coal than that of the Blind Canyon coal and the tendency for TBAH to react with these functional groups<sup>6</sup>.

### Comparison of MoS<sub>3</sub> and ATTM catalysts for pretreatment

Table 5 shows the conversion data of thermal (non catalytic) and catalyst-impregnated coals. The conversions of coals with both catalysts are greater than those obtained without catalyst. ATTM effectively enhances preasphaltenes and asphaltenes formation for both coals and also improves oil yield for Blind Canyon coal (DECS-6), but not for of the Texas lignite (DECS-1). MoS<sub>3</sub> improved only preasphaltene yield for the Texas lignite; it has not affected formation of asphaltenes and of oil. For the Blind Canyon coal with MoS<sub>3</sub>, preasphaltenes were 8% greater than those obtained without catalyst. This yield was even higher than obtained with ATTM, and greater conversion was obtained than with ATTM. However, oil yield was not improved with MoS<sub>3</sub>. The conversion of Illinois #6 coal with MoS<sub>3</sub> was found to be comparable to that obtained with ATTM<sup>7</sup>. ATTM was reacted at 275°C under hydrogen atmosphere (1000 psi cold) without coal in order to determine the fate of ATTM at the preliquefaction conditions used in this work. Elemental analysis of the product shows 3.26% of nitrogen (Table 2). The different activities of these catalysts with both coals, may be due to dependence of dispersion on the type of coal and on the destructive effect of ammonia, released from decomposition of ATTM, on catalytic activity of molybdenum sulfide catalyst.

### The effect of preswelling on liquefaction

The conversion results of solvent swollen coals without catalyst impregnation are given in Tables 6 and 7. The treatment with methanol enhanced oil formation, decreased preasphaltenes and asphaltenes for the Texas lignite (DECS-1); enhanced oil and preasphaltenes, decreased asphaltenes for the Blind Canyon coal (DECS-6). THF is the least effective swelling reagent in terms of liquefaction of the Texas lignite. It

provided great conversion with its high swelling ability for the Blind Canyon coal ( $Q=1.9$ ). THF pretreatment increased total conversion of the Blind Canyon coal from 17.7% to 22.1% and oil formation from 4.9% to 9.2%, but its effect on formation of preasphaltenes is not significant and did not influence formation of asphaltenes. The pyridine pretreatment provided greater total conversion and oil formation for the Texas lignite than those obtained from methanol- and THF- treated coals. However, this treatment diminished formation of preasphaltenes for this coal. The pyridine treatment for Blind Canyon coal, surprisingly, decreased total conversion from 17.7% to 16.0%, formation of preasphaltenes from 10.7% to 6.4%, asphaltenes from 2.1% to 1.3%, but increased formation of oil from 4.9% to 9.2%. TBAH treatment provided the highest conversion for the both coals relative to the other solvents, even though 10% TBAH solution in 1:1 water:methanol mixture swelled the Blind Canyon coal least. There might be two reasons for the high conversion with TBAH addition onto coals. The first is the swelling effect. The evaporation of methanol and water from mixture increases the concentration of TBAH. The TBAH thus, concentrated by evaporation can increase the level of swelling of the coal, even for Blind Canyon. Second, in a reaction of 40% TBAH in a tubing bomb at the same reaction conditions as pretreatment experiments (but without coal), butane and butene were observed in the gaseous products. It can be expected that TBAH likely transformed to amine compounds. Therefore, TBAH is going to act as a solvent precursor. It has been found that amines are very good promoters for coal liquefaction<sup>8-9-10</sup>. The nitrogen contents of residue, preasphaltenes and asphaltenes were found to be higher for TBAH-swollen coal than those of unswollen coal. This increase can be attributed to incorporation of amines. Therefore, assuming that TBAH transformed to tributylamine, the amount of tributylamine incorporated in residue, asphaltenes and preasphaltenes can be determined from their difference of nitrogen content and those of the respective products from unswollen coal (Table 10). Incorporation of tributylamine in the residue of the Texas lignite is greater than in Blind Canyon, and addition of catalyst increased this incorporation. Addition of TBAH provided the highest increase in yields of preasphaltenes, asphaltenes and oil for the Texas lignite compared to those of coals swollen with other solvents. For the Blind Canyon coal, TBAH addition provided the greatest conversion, yields of preasphaltenes and asphaltenes, but a lower yield of oil relative to those for coals swollen with the other solvents. For the Texas lignite, conversion without catalyst increased in the order of none < THF < methanol < pyridine < TBAH. For the Blind Canyon coal conversion without catalyst increased in the order of pyridine < none < methanol < THF < TBAH. The extractive ability of a particular solvent is related to the swelling effect of that solvent for a particular coal. A good extractive solvent can disrupt weak bonds in the coal network or in material trapped in the coal structure. Therefore, the molecules released by this disruption and the weakened structure can be liquefied at less severe conditions.

Comparative conversion data of ATTM-impregnated swollen Texas lignite and Blind Canyon are given in Tables 8 and 9. For the Texas lignite with ATTM catalyst the effect of swelling on formation of preasphaltenes and asphaltenes decreases, except for TBAH. The greatest conversions and formation of all types of products were obtained with TBAH addition. If these data were compared with those obtained without catalyst, it can be seen that addition of ATTM increased total conversion and formation of preasphaltenes and asphaltenes, but did not change the amount of oil. The order of conversion can be given as none < THF, methanol < pyridine < TBAH for the Texas lignite. For the Blind Canyon coal methanol treatment decreased yield of asphaltenes, but did not affect conversion and yields of other products. THF treatment decreased formation of preasphaltenes and asphaltenes, while it provided the greatest yield of oil relative to other solvents. However, THF treatment did not affect total conversion. Pyridine treatment decreased formation of preasphaltenes and asphaltenes while increasing total conversion and formation of oils. TBAH addition seemed to decrease the activity of the molybdenum sulfide catalyst, because the conversion of TBAH-treated coal was less than unswollen coal. The addition of ATTM to swollen coals increased significantly total conversion and formation of yields for the Blind Canyon coal except TBAH added coal. The order of conversion is noticed as TBAH < none, methanol, THF < pyridine

## CONCLUSIONS

Without swelling pretreatment, impregnation of both coals increased conversion at 275°C. The increased conversion was mainly a result of an increased yield of preasphaltenes. In the absence of catalyst, swelling the Texas lignite before liquefaction improves conversion, with the increase mainly a result of additional (oil+gas) yield. The relative effectiveness of various solvents for improving conversion is in the same general order as their effectiveness at swelling the coal. Preswelling with methanol or

pyridine has little effect on liquefaction of the Blind Canyon coal, but both THF and TBAH provide increased conversion, as a result of improved preasphaltene yields. With this coal, the effectiveness of solvents at improving liquefaction is not in the same order as their ability to swell the coal. The combined effect of catalyst addition and swelling is to enhance conversion of the lignite, with a doubling of conversion obtained by impregnation with ATTM and swelling by TBAH. The yields of all products are enhanced by this pretreatment. In contrast, little improvement in total conversion of the Blind Canyon coal is obtained by combining ATTM impregnation and solvent swelling, but changes in the relative proportions of the products can be obtained.

## ACKNOWLEDGEMENTS

The authors are grateful for the financial support provided for this work by the U. S. Department of Energy. The authors are also pleased to acknowledge useful discussions with Dr. J. T. Joseph of the Amoco Corporation.

## REFERENCES

1. Hombach, H. P., Fuel, 1981, 60, 663.
2. Given, P. H. Marzec, A., Barton, W. A., Lynch, L. J., Gerstein, B.S., Fuel, 1986, 65, 155.
3. Rincon, J. M., and Cruz, S., Fuel, 67, 1162.
4. Joseph, J. T., Beneficial effects of preswelling on coal liquefaction, Fuel, in press.
5. Naumann, A. W., United States Patent, 1981, 4243554.
6. Liotta, R., Rose, K., and Hippo, E., J. Organic Chemistry, 1981, 46, 277.
7. Utz, B. R., Cugini, A. V. and Frommell, E. A., Preprints Div. Fuel Chem., Am. Chem. Soc., 1988, 34(4), 1423.
8. Kazimi, F., Chen, W. Y., Chen, J. K., Whitney, R. R., Zimny, B., Preprints Div. Chem. Am. Chem Soc., 1985, 30(4), 402.
9. Tagaya, H., Sugai, J., Onuki, M. and Chiba, K., Energy & Fuel, 1987, 1, 397.
10. Miller, R. L., Baldwin, R. M. and Kennar, D. R., Preprints Div. Chem. Am. Chem. Soc., 1990, 35(1), 9.

Table 1. Characteristics of coals.

<u>Sample No.</u>	<u>PSOC-1444</u>	<u>PSOC-1503</u>	<u>DECS-1</u>	<u>DECS-6</u>
Seam	Unnamed	Blind Canyon	Bottom	Blind Canyon
County	Freestone	Emery	Freestone	Emery
State	Texas	Utah	Texas	Utah
Province	Gulf	Rocky Mt.	Gulf	Rocky Mt.
Sampling Date	3/30/85	10/01/85	12/11/89	6/07/90
ASTM rank class	Lignite	hVC b	Sub	hVB b
Moisture Content % wt	31.91	10.35	30.00	4.73
Min. Matter % wt (dry)	19.02	4.36	17.97	6.67
<u>Elem. Comp. (% dmmf)</u>				
C	76.21	80.80	76.13	81.72
H	4.71	6.12	5.54	6.22
N	1.42	1.55	1.5	1.56
S (org)	1.36	0.54	1.05	0.40
O (diff)	16.29	10.58	15.78	10.10

Table 2. Elemental analysis of ATTm, MoS<sub>3</sub> and the product obtained from microautoclave reaction of ATTm at 1000 psi (cold) hydrogen gas at a temperature of 275 °C.

Catalyst	%N	%H	%Mo	%S	%H <sub>2</sub> O	nS:nMo
ATTm	10.81	3.10	37.01	49.15	ND	3.98
MoS <sub>3</sub>	ND	ND	44.45	50.50	1.39	3.41
HATTm*	3.26	1.40	49.74	39.40	6.36	2.38

ND = Not determined.

\* = Hydrogenated ATTm

Table 3. Change in solvent swelling ratio (Q) with time for the Texas Lignite (PSOC-1444).

Methanol		THF		Pyridine		TBAH	
Time (h)	Q	Time (h)	Q	Time (h)	Q	Time (h)	Q
5.0	1.1	6.0	1.2	6.5	1.6	6.0	2.6
11.5	1.1	16.5	1.2	21.5	1.6	14.5	2.6
23.0	1.1	22.0	1.3	42.0	1.6	24.5	2.7
27.5	1.1	28.0	1.3				

Table 4. Change in solvent swelling ratio (Q) with time for the Blind Canyon hvCb coal (PSOC-1503).

Time (h)	Methanol Q	THF Q	Pyridine Q	TBAH (10%) Q
6.0	1.2	1.9	2.4	1.2
10.0	1.3	1.8	2.3	1.2
20.0	1.3	1.8	2.2	1.2
26.0	1.3	1.8	2.3	1.2

Table 5. The activity of ATTm and MoS<sub>3</sub> on liquefaction of (Texas lignite) DECS-1 and (Blind Canyon hvB) DECS-6 coals at 275°C.

Coal	Catalyst	Conversion % (daf)			
		Total	Preasph.	Asphal.	Oil + Gas
DECS-1	None	6.6	2.8	2.2	1.6
"	ATTm	9.0	3.9	3.6	1.5
"	MoS <sub>3</sub>	7.2	3.9	1.7	1.6
DECS-6	None	17.7	10.7	2.1	4.9
"	ATTm	25.0	15.1	3.0	6.9
"	MoS <sub>3</sub>	26.9	19.0	3.3	4.6

Table 6. Effect of preswelling treatment on liquefaction of Texas lignite (DECS-1) at 275°C.

Sol. Treat.	Conversion %(daf)			
	Total	Preasphalt.	Asphal.	Oil +Gas
None	6.6	2.8	2.2	1.6
Methanol	8.4	2.2	1.8	4.4
THF	7.4	2.9	0.9	3.6
Pyridine	10.0	1.7	2.0	6.4
TBAH	17.5	5.2	3.9	8.4

Table 7. Effect of preswelling treatment on liquefaction of Blind Canyon hvB (DECS-1) at 275°C.

Sol. Treat.	Conversion %(daf)			
	Total	Preasphalt.	Asphal.	Oil +Gas
None	17.7	10.7	2.1	4.9
Methanol	19.8	12.2	1.6	6.0
THF	22.1	11.1	2.2	9.2
Pyridine	16.0	6.4	1.3	8.2
TBAH	24.0	15.1	3.6	5.3

Table 8. Effect of preswelling on liquefaction of Texas Lignite with ATTM catalyst at 275°C.

Sol. Treat.	Conversion %(daf)			
	Total	Preasphalt.	Asphal.	Oil+Gas
None	9.0	3.9	3.6	1.5
Methanol	9.5	2.8	2.2	4.5
THF	9.3	3.1	2.8	3.4
Pyridine	11.8	2.9	2.4	6.5
TBAH	18.7	6.2	4.6	7.9

Table 9. Effect of preswelling on liquefaction of Blind Canyon hvB with ATTM at 275°C.

Sol. Treat.	Conversion %(daf)			
	Total	Preasphalt.	Asphal.	Oil + Gas
None	25.0	15.1	3.0	6.9
Methanol	24.7	15.4	2.4	6.9
THF	25.1	12.4	2.4	10.3
Pyridine	26.7	14.6	2.6	9.5
TBAH	23.7	13.5	3.9	6.3

Table 10. The percentage of tributyl amine incorporated to residue, preasphaltenes and asphaltenes of TBAH treated Texas lignite (DECS-1) and Blind Canyon hvB (DECS-6) after hydrogenation with or without ATTM.

Coal	ATTM	Incorporation of TBAH %(dry)		
		Residue	Preashalt.	Asphal.
DECS-1	No	3.2	4.7	5.0
DECS-1	Yes	4.3	3.8	5.5
DECS-6	No	1.7	2.1	8.6
DECS-6	Yes	4.3	3.8	5.5